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HOMOGENEITY CONTROL IN HETEROGENEOUS MATERIALS (A REVIEW)

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An analysis of the methods most suitable for ceramics technology for controlling the homogeneity of component distribution in mixtures and the distribution of the porosity (or heterogeneous components) over the article volume is made. A rather rigorous and simple method for evaluation of mixture (sample) homogeneity is suggested that is based on a hierarchic approach and statistical evaluation of the accuracy of determining the concentration of a key component in mixture samples.

Development and production of high-quality materials from heterogeneous mixtures is related to providing and controlling the homogeneity of component distribution in mixtures and the distribution of the porosity and heterogeneous components in the material (sample) [1 – 6]. Thus, the quality of blending of powders has a substantial effect on the homogeneity of the chemical composition of the mixture and the finished material produced from this mixture. Inhomogeneity of the porous structure of the intermediate product impairs the service properties of the finished product.

The homogeneity of a mixture of powder materials is determined primarily by the mixing conditions (duration, type of equipment, introduction of auxiliary elements, such as balls, etc.). Various aspects of the blending process are considered in [1, 2].

It is convenient to test the operation of the blending equipment and evaluate the effect of the mixing duration on the mixture homogeneity using a magnetic material, such as nickel, as one of the powder materials, since the latter can easily be isolated from a mixture sample using a magnetic field.

It is expedient to accompany any study in ceramic technology and powder metallurgy with a study of the volume distribution of a certain parameter, for example, the density. Analysis of the density distribution is one of the main methods of quality control used to test articles produced by various technologies.

In studying the density distribution [1], the finished product is cut into cubes of equal volumes, after which the

average density of each cube is determined, for instance, by hydrostatic weighing. The merit of the method consists in its simplicity and availability, whereas its drawbacks include high labor input, the averaged nature of the resulting data, the feasibility of this method only for samples and models of substantial sizes, and, finally, which is most important, the fact that the product is destroyed in testing.

Of special interest are methods for analysis and control of the homogeneity of materials that are based on computer scanning of the sample surface in combination with computerized statistical processing of the scanning data [4]. However, these methods require highly skilled personnel and complicated instruments.

The most promising are nondestructive methods of control [7], whose main parameters are the sensitivity (determined by size of the smallest defects and inhomogeneities identified) and the resolution (determined by the least distance between two neighboring separately identified defects).

Determination of the density or porosity distribution by nondestructive methods based on recording of the attenuation of x-ray or gamma radiation passing through the article is complicated and requires bulky and expensive equipment, trained personnel, and a specialized laboratory. Moreover, the intensity of radiation passing through a sample can vary due to uncontrolled inhomogeneity of the composition, which is possible in articles made of multicomponent mixtures.

The advantages of these methods consist in their being contact-free and having a high measurement rate with a high

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resolution. Thus, in [8] a relative error in porosity control of 3% was obtained with a beam diameter of 2 mm.

As a simple and available method, free of the above drawbacks, for studying the density distribution in porous materials it is suggested in [9] that the pores of the sample or article be filled with a luminophor and the article be placed under a source of ultraviolet radiation. The luminescence brightness distribution observed here corresponds to the porosity distribution in the article. The work shows that the proposed method of quantitative and qualitative analysis of the density distribution is simple and reliable and does not require specialized instruments. It can be used to study the regularities of the sintering process in nondestructive control of the quality of a porous article.

Visual study of the luminescence of porous bodies impregnated with a luminophor can be recommended as a rapid method for testing product quality, especially structural articles produced by technologies of ceramic or powder metallurgy under industrial conditions. Luminescence photographed or measured photometrically in any direction directly from the sample makes it possible to obtain a density distribution curve for the article.

The luminescent agent can be a finely disperse luminophor powder rubbed into the article surface or an impregnating luminescent liquid. Impregnation of an article with a liquid luminophor is carried out in a vacuum of about 2.7 Pa (0.02 Torr) for 30–40 min.

It is assumed in the above-described method (as in the commonly used method of determining density by hydrostatic weighing) that the sample does not contain closed pores and the impregnating liquid fills all the cavities between the particles. It should be noted that additional weighing of the impregnated sample in air and in water makes it possible, knowing its initial weight, to determine immediately the average density from the relationship

$$\rho_k = m_1 / [(m_1 - m_3) / \rho_w - (m_2 - m_1) / \rho_l],$$

where m_1 and m_2 are the weight of the nonimpregnated and impregnated sample; m_3 is the weight of the impregnated sample in water; ρ_l and ρ_w are the density of the impregnating liquid and water.

The calibration curve is a power function of the type $y = x^{3/2}$. In fact, the blackening of film is proportional to the pore area or, roughly, the square of the pore linear size, and the porosity is proportional to the pore linear size to the power 1/3. It follows from the curve that the method is most sensitive in the range of medium porosity values.

A curve is constructed for the selected luminophor that reflects the relationship between the degree of film blackening (or the relative luminescence brightness) and the porosity. The constructed dependence then can be used for quantitative study of the porosity in any porous articles. Thus, the application of this method to determine the local porosity in a sample of vanadium boride confirmed the assumption of a small spread in porosity values for such a sample.

The distribution of a certain component in an article or the initial mixture as a function of the amount of it and the blending duration is studied in [10] using a radioactive isotope. The efficiency of the method is demonstrated using the example of the sulfur distribution in iron powder used to produce plain bearings, and the optimum blending duration is established.

The studies were performed using the radioactive sulfur isotope S35 with a half-life of 87.1 days and a beta-radiation energy of 0.167 MeV. Sulfur powder with a fractional composition of less than 120 μm was used. Autoradiographic and radiometric methods allowed for rapid determination of the degree of homogeneity of the mixture and the finished product before and after sintering. The quantity of radioactive sulfur introduced into the mixture was calculated from the condition that a radiation intensity in the interval of 400–600 pulse/(min · cm²) can produce an autoradiographic image on photoplates of MR type. A radiation intensity of 500 pulse/(min · cm²) was taken as the optimum value.

The mixture and the samples were prepared in the following way. A mixture batch of 500 g consisting of iron powder, elementary sulfur powder, and the calculated amount of radioactive isotope S35 was poured into a conical mixer, filling it to 1/3 of its volume. The rotational speed of the agitator was 40 min⁻¹. Thus, 24 mixture batches were prepared with a sulfur content of 0.25, 0.5, 1.0, and 2.0%. The mixing duration of each batch was 30, 60, 90, 120, 180, and 240 min. Ten 2 g samples were taken from different sites of the prepared mixture. The samples were weighed on an analytical scale (precision up to 0.0002 g). Then the samples were placed in cassettes made of organic glass with cavities made to contain the mixtures. The intensity of the radioactive irradiation of the samples was measured on a special device with a counter at the end. The degree of homogeneity of the mixtures was inferred from their activity. The samples of the mixtures produced by 30 min agitation had either low or high activity, which indicated substantial inhomogeneity of the prepared mixture. As the mixing duration increased, the activity of the samples gradually became more uniform.

Each batch was used to prepare samples shaped as rings with outer diameter 40 mm, inner diameter 17 mm, and height 12 mm. The samples were compressed on a hydraulic press at a pressure of 500 MPa (5 ton/cm²). The quality of the upper and lower punch surface made it possible to obtain autoradiograms of samples before sintering without special surface treatment.

It should be noted that the quality of the mixing depends on the concentration of the target component. Thus, the activity of the mixture samples with 1 and 2% sulfur after 2 h mixing points to uniform distribution of the sulfur, and the samples of mixtures with 0.25 and 0.5% sulfur exhibit a substantial spread in activity, which points to nonuniform distribution of the sulfur for the adopted mixing time (homogeneity of the sulfur distribution for the indicated amounts of sulfur in the mixture is reached only after 3 h agitation). This is

confirmed by the autoradiograms of the samples before sintering.

Paper [11] suggests a method for monitoring the quality of mixing and mixture homogeneity (powder materials and removable pore-forming agent) of permeable materials based on the inhomogeneity coefficient

$$K = \frac{r_{cr} - r}{r},$$

where r_{cr} is the breakdown radius determined from mercury of gas-liquid porometry; r is the average pore radius found from the material permeability or from gas-liquid porometry [12].

Determination of the local penetrability can be used to control the homogeneity of the porous structure of filter materials. The most convenient is use of a sensor in the form of a semiconductor ball 0.6 mm in diameter heated by direct current [3] (the sensor resistance changes with change in the rate of a cooling local air flow after its passes through the sample). The sensor is calibrated beforehand, for example, based on the change in its resistance at the center of a pipe, using a laminar air flow with a prescribed flow rate. It is taken into account that the maximum air rate at the center of the pipe is twice the average rate. The sensor is fixed at a distance of 0.5 – 1.0 mm from the filter surface. If the air temperature is maintained within an interval of $\pm 5^\circ\text{C}$, the calibration does not change for 2 – 3 weeks. Usually the central part of the samples is more penetrable.

If the permeable material is conducting, it is possible to evaluate the inhomogeneity of its porosity over its thickness taking into account the features of vortex currents passing through the material [13].

Since the initial powder materials are usually polydisperse systems, their granulometric composition affects the quality of mixing. An unbiased result of analysis of mixture homogeneity depends on the method of analysis and data processing.

The reliability of determination of the concentration of the target component in samples depends to a great extent on the number of particles (or pores) in the mixture samples (or the article specimens). The minimum volumes of the samples (specimens) used in the analysis are usually determined under the condition that for a confidence reliability of 0.99 and a number of target-component particles of more than 200, the deviation from the general sampling does not exceed 1.5% [1]. That is, in order to determine the degree of inhomogeneity it is desirable that the samples contain at least 200 target-component particles (or pores in the portion of the article).

With a lower content of the target component, when the volumes of the analyzed samples and specimens (or portions of the article) are small and the number of particles (pores) in them is a random quantity, it is necessary to take into account the effect of the randomness on the error of the determination.

An expression for the variance of the target-component content in monodisperse samples for ideal mixing is offered in [1]:

$$S'^2 = p(1-p)/N,$$

where p is the fraction of the target component in the sample; N is the number of particles in the sample.

For bidisperse systems this expression can be modified in the following way:

$$S'^2 = 2p(1-p) \left[V(\bar{D}^3 + \bar{d}^3) \right]^{-1},$$

where V is the sample volume; \bar{D} is the mean diameter of the target component in the sample; \bar{d} is the mean diameter of the other components in the sample.

Finally for assessing the quality of the mixing (the homogeneity of the mixture) we obtain

$$v = \frac{1}{C} \left\{ (n_i - 1)^{-1} \sum_{i=1}^n (C_i - C)^2 - \frac{2p(1-p)}{\left[V(\bar{D}^3 + \bar{d}^3) \right]^{0.5}} \right\},$$

where v is the coefficient of variation; n is the total number of selected samples; C_i is the concentration of the target component in the i -th sample; C is the mean concentration of the target component in the mixture.

The considered approach to evaluating the homogeneity of mixtures does not make it possible to evaluate its accuracy. Therefore, we propose a more rigorous and rather simple method for evaluating the homogeneity of mixtures (specimens) that is based on a hierarchical approach and statistical evaluation of the accuracy of determining the target-component concentration in mixture samples (root-mean-square error, confidence interval, and confidence probability).

The evaluation is made in the following way. A certain number of samples n (not less than 3) of the material are taken. The samples are divided into $n_{i,j}$ parts (usually $n_{i,j} = 3$ is sufficient), and the content of the target component $C_{i,j}$ is determined in each part. Next, the mean concentrations C_j in the samples, the concentration of the target component in the whole mixture C , and the concentration variation coefficient (the mixture inhomogeneity coefficient) are calculated:

$$C_j = n_{i,j}^{-1} \sum_{i=1}^{n_{i,j}} (C_{i,j}); \quad C = n_j^{-1} \sum_{j=1}^n (C_j);$$

$$v = \frac{1}{C} \left[(n_j - 1)^{-1} \sum_{j=1}^{n_j} (C_j - C)^2 \right]^{0.5},$$

where C_j is the mean concentration of the target component in the j -th mixture sample; $n_{i,j}$ is the number of parts in the

j -th mixture sample; $C_{i,j}$ is the target component concentration in the i -th part of the j -th sample.

After that the root-mean-square error in determining the concentration S_j for all the samples and the whole mixture S is calculated from the expressions

$$S = n^{-1} \sum_{j=1}^n S_j;$$

$$S_j = \left[(n_{i,j} - 1)^{-1} \sum_{i=1}^{n_{i,j}} (C_{i,j} - C_j)^2 \right]^{0.5}.$$

The confidence interval is usually determined by a value not exceeding 0.1 – 0.3 times the systematic component of the variation error. The reliability (for a given confidence interval) is determined by the standard method using the Student distribution:

$$\Delta_j < t(\alpha, n_{i,j}) S_j / (n_{i,j})^{0.5},$$

where Δ_j is the confidence interval; $t(\alpha, n_{i,j})$ are the Student coefficients; α is the reliability (the confidence probability).

Since the precision of mixture inhomogeneity evaluation increases with decreasing volume of the samples, the number of particles in them is a random quantity. It should be taken into account that the larger the sample volume, the lower the sensitivity of the determination. We calculate the minimum number of particles of the target component in the sample parts taking the root-mean-square error of the calculation due to the random variations of the number of particles in the sample parts equal to 1%, the confidence interval equal to $\Delta C = 0.5\%$, and the reliability equal to $\alpha = 0.99$. Using a table presenting the dependence of the number of tests on the ratio of the length of the confidence interval to the root-mean-square error and the confidence probability [14], we obtain the result that the minimum number of particles or pores n' in a part of a sample (specimen) should be at least 31. Therefore, the whole sample should contain at least 93 particles. If a lower reliability, 0.95, is sufficient, the number n' should be at least 18.

Thus, in monitoring the homogeneity of component distribution in mixtures and the distribution of the porosity (or

heterogeneous components) over the article material volume, one should take into account the representation of the fractions (the number of particles or pores in them). It is also expedient to indicate the volume of the mixture and the samples.

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